

APPENDIX B

Test Methods

APPENDIX B

Test Methods

Vehicle exhaust sampling was carried out at ARB's facility in El Monte, using dynamometer test cell #1. For this program, the USA three-phase driving cycle was employed. This driving cycle is composed of a cold transient phase, a stabilized phase, and a hot transient phase. The sampling procedures were conducted according to the Federal Test Procedure (FTP) as specified in the Code of Federal Regulations, Title 40, Part 86.

Emissions data consist of the following:

- (1) Non-methane organic gases (NMOG) as determined by ARB Methods Nos. 1001 (alcohols), 1002 (light hydrocarbons), 1003 (mid-range hydrocarbons), and 1004 (carbonyls)
- (2) Methane, carbon monoxide, carbon dioxide, oxides of nitrogen, and total hydrocarbons as determined by continuous monitoring instrumentation from three bag samples collected during each phase of the test cycle
- (3) Nitrous oxide, nitrous acid, and methyl nitrite as determined by an on-line Fourier Transform Infrared Analyzer.

Three Tedlar bags were used to collect time-integrated samples during each phase of the test cycle. The continuous monitoring instruments were valved to each bag following the test run and concentrations were recorded.

Transfer bags were used to remove a portion of exhaust from each bag. These secondary bags were transferred to the analytical laboratory for subsequent analysis of the light (Method 1002) and mid-range hydrocarbons (Method 1003).

Alcohols (Method 1001) were determined using on-line impingers. Carbonyl species (Method 1004) were determined using on-line impingers prior to January 22, 1993, and using Sep-Pak cartridges thereafter. Time-integrated samples were obtained for each phase of the test cycle.

The FTIR instrument was connected on-line. For nitrous oxide, measurements were made in real time as well as in a "static" mode (sample from the Tedlar bag) because of interference from high transient concentrations of carbon monoxide during real time monitoring. The concentration values reported were based on calibrations and procedures established by the instrument manufacturer. ARB staff are currently developing additional quality control procedures which will become part of the laboratory's standard operating procedure for this analysis. As a result, the FTIR-based method and results should be considered developmental.

VEHICLE EMISSIONS

In the first quarter of 1993, ARB changed its operating procedures for gas chromatography to increase sample throughput, to improve chromatographic resolution, and to increase the number of identifiable peaks. The more significant changes were:

1. The GCs used for the light-end and mid-range hydrocarbons (Methods #1002 and 1003) were automated so that bag samples could be analyzed without operator interface.
2. Temperature programming conditions were also changed to improve resolution of normally co-eluting compounds. This change also resulted in the identification of several previously labelled unknown species.
3. For Method #1004 (carbonyls), silica gel cartridges coated with 2,4-dinitrophenylhydrazine (DNPH) reagent were implemented. Previously, DNPH impinger solution was used. The list of identifiable species was also expanded.
4. The data acquisition/processing was changed to allow for more automated operations to be conducted.

The first analytical procedures were used for tests conducted from November 1992 through January 1993. The new procedures were employed beginning in March 1993. Table B-1 shows a listing of the target species measured by ARB during the vehicle exhaust tests conducted in the fourth quarter of 1992. The expanded list for 1993 is shown in Table B-2.

Table B-1. Species Targeted by the ARB During Vehicle Testing Conducted in the Fourth Quarter of 1992

| Light-End Hydrocarbons (MLD Method #1002) |
|--|
| Ethane |
| Ethene |
| Propane |
| Ethyne |
| Methylpropane |
| Butane |
| Propene |
| Methylbutane |
| Pentane |
| 1-Butene |
| 2-Methylpropene |
| Mid-Range Hydrocarbons (MLD Method #1003) |
| t-2-Butene |
| 1-Butyne |
| c-2-Butene |
| 3-Methyl-1-butene |
| 2-Methylbutane |
| 1-Pentene |
| 2-Methyl-1-butene |
| 1,3-butadiene |
| 2-Methyl-1,3-butadiene |
| t-2-Pentene |
| C ₆ H ₁₂ Alkene |
| c-2-Pentene |
| 2-Methyl-2-butene |
| 2,2-Dimethylbutane |
| Cyclopentene |
| 4-Methyl-1-pentene |
| Cyclopentane |
| 2,3-Dimethylbutane |
| C ₆ H ₁₂ Alkene 1 |
| 2-Methylpentane |
| C ₆ H ₁₂ Alkene 2 |
| 3-Methylpentane |
| C ₆ H ₁₂ Alkene 3 |
| n-Hexane |
| 3-Hexene |
| t-2-Hexene |
| C ₆ H ₁₂ Alkene 4 |

VEHICLE EMISSIONS

| |
|---------------------------------|
| c-2-Hexene |
| C6H12 Alkene 5 |
| Methylcyclopentane |
| C6H12 Alkene 6 |
| 2,4-Dimethylpentane |
| C7H16 Alkane |
| Benzene |
| 3-Methyl-1-hexene |
| Cyclohexane |
| 2-Methyl-3-hexene |
| 4-Methyl-2-hexene |
| 2-Methylhexane +Dimethylpentane |
| C6H10 Cycloalkene |
| 3-Methylhexane |
| C7H14 Alkene |
| Dimethylcyclopentane |
| 2,2,4-Trimethylpentane |
| n-Heptane |
| C7H12? Cycloalkene |
| Methylcyclohexane |
| Trimethylcyclopentane |
| Dimethylhexane |
| C8H18 Alkane |
| Trimethylcyclopentane 1 |
| 2,3,4-Trimethylpentane |
| Toluene |
| 2,3-Dimethylhexane |
| Methylheptane |
| Unidentified 1 |
| Dimethylcyclohexane |
| 2,2,5-Trimethylhexane |
| Ethylmethylcyclopentane |
| n-Octane |
| C8H16 Cycloalkane |
| 2,3,5-Trimethylhexane |
| NNDime-acetamide |
| C8H14? Cycloalkene |
| Dimethylheptane |
| C9H18 Alkene |
| Ethylbenzene |
| Trimethylcyclohexane |
| m & p-Xylenes |
| C9H20 Alkane |

VEHICLE EMISSIONS

| |
|-------------------------------------|
| Styrene |
| Trimethylheptane |
| o-Xylene |
| C10H22 Alkane 1 |
| C9H18 Alkene 1 |
| n-Nonane |
| Ethylmethylcyclohexane |
| i-Propylbenzene |
| C10H22 Alkane 2 |
| Dimethyloctane |
| n-Propylbenzene |
| 3-Ethyltoluene |
| 4-Ethyltoluene |
| 1,3,5-Trimethylbenzene |
| C10H22 Alkane 3 |
| 2-Ethyltoluene |
| C10H22 Alkane 4 |
| 1,2,4-Trimethylbenzene |
| n-Decane |
| n-Undecane |
| C10H14 Aromatic |
| Alcohols (MLD Method #1001) |
| Methanol |
| Ethanol |
| Carbonyls (MLD Method #1004) |
| Formaldehyde |
| Acetaldehyde |
| Acrolein |
| Acetone |
| Propionaldehyde |
| Butanal |
| Benzaldehyde |
| Hexanal |

VEHICLE EMISSIONS

**Table B-2. Species Targeted by the ARB During
Vehicle Testing Beginning the
First Quarter of 1993**

| Light-End Hydrocarbons (MLD Method #1002) |
|--|
| Ethane |
| Ethene |
| Propane |
| Propene |
| Methylpropane |
| Ethyne |
| n-Butane |
| Propadiene |
| Trans-2-butene |
| 1-Butene |
| 2-Methylpropene |
| cis-2-Butene |
| 2,2-Dimethylpropane |
| Methylbutane |
| 1-Propyne |
| n-Pentane |
| 1,3-Butadiene |
| 3-Methyl-1-butene |
| Cyclopentene |
| Trans-2-pentene |
| 2-Methyl-2-butene |
| 1-Pentene |
| 2-Methyl-1-butene |
| cis-2-Pentene |
| 1-Buten-3-yne |
| 2-Butyne |
| 1-Butyne |
| Mid-Range Hydrocarbons (MLD Method #1003) |
| 2-Methyl-1,3-butadiene |
| 3,3-Dimethyl-1-butene |
| 1,3-Pentadiene |
| Cyclopentadiene |
| 2,2-Dimethylbutane |

VEHICLE EMISSIONS

| |
|------------------------------|
| 3-Methyl-1-pentene |
| Cyclopentane |
| 2,3-Dimethylbutane |
| 1-Methyl-tert-butyl-ether |
| 2-Methylpentane |
| 4-Methyl-cis-2-pentene |
| 3-Methylpentane |
| 2-Methyl-1-pentene |
| n-Hexane |
| Trans-3-hexene |
| Trans-2-hexene |
| 2-Methyl-2-pentene |
| 3-Methylcyclopentene |
| cis-2-Hexene |
| 3-Methyl-c-2-pentene |
| 2,2-Dimethylpentane |
| Methylcyclopentane |
| 2,4-Dimethylpentane |
| 2,2,3-Trimethylbutane |
| 3,4-Dimethyl-1-pentene |
| 1-Methylcyclopentene |
| Benzene |
| 3-Methyl-1-hexene |
| 3,3-Dimethylpentane |
| Cyclohexane |
| 4-Methyl-t-2-hexene |
| 2-Methylhexane |
| 2,3-Dimethylpentane |
| Cyclohexene |
| 3-Methylhexane |
| 1-Heptene |
| Trans-1,2-dimethylpentane |
| cis-1,3-Dimethylcyclopentane |
| 3-Ethylpentane |
| 2,2,4-Trimethylpentane |
| 3-Methyl-trans-3-hexene |
| n-Heptane |

VEHICLE EMISSIONS

| |
|------------------------------------|
| 2-Methyl-trans-2-hexene |
| Trans-2-heptene |
| 2-Methyl-cis-2-hexene |
| cis-2-Heptene |
| 2,4-Dimethyl-2-pentene |
| Methylcyclohexane |
| 2,2-Dimethylhexane |
| 2,4,4-Trimethyl-2-pentene |
| 2,5-Dimethylhexane |
| 2,4-Dimethylhexane |
| 3,3-Dimethylhexane |
| 2,3,4-Trimethylpentane |
| Toluene |
| 2,3,3-Trimethylpentane |
| 2,3-Dimethylhexane |
| 2-Methylheptane |
| 3-Methylheptane |
| 2,2,5-Trimethylhexane |
| 1-Methyl-trans-3-ethylcyclopentane |
| Octenes |
| n-Octane |
| Trans-2-octene |
| Trans-1,3-dimethylcyclohexane |
| cis-2-Octene |
| 2,3,5-Trimethylhexane |
| 2,4-Dimethylheptane |
| 2,6-Dimethylheptane |
| 3,5-Dimethylheptane |
| Ethylbenzene |
| 2,3-Dimethylheptane |
| m- & p-Xylene |
| 4-Methyloctane |
| 3-Methyloctane |
| Styrene (ethenylbenzene) |
| o-Xylene |
| 2,2,4-Trimethylheptane |
| 1-Methyl-4-ethylcyclohexane |

VEHICLE EMISSIONS

| |
|--|
| n-Nonane |
| (1-Methylethyl)Benzene |
| 2,2-Dimethyloctane |
| 2,5-Dimethyloctane |
| 2,4-Dimethyloctane |
| 2,6-Dimethyloctane |
| n-Propylbenzene |
| 1-Methyl-3-ethylbenzene |
| 1-Methyl-4-ethylbenzene |
| 1,3,5-Trimethylbenzene |
| 1-Methyl-2-ethylbenzene |
| 1,2,4-Trimethylbenzene |
| n-Decane |
| (2-Methylpropyl)Benzene |
| (1-Methylpropyl)Benzene |
| 1-Methyl-3-(1-Methylethyl)Benzene |
| 1,2,3-Trimethylbenzene |
| 1-Methyl-4-(1-Methylethyl)Benzene |
| 2,3-Dihydroindene (indan) |
| 1,3-Diethylbenzene |
| 1-Methyl-2-(1-Methylethyl)Benzene |
| 1,4-Diethylbenzene |
| 1-Methyl-3-n-propylbenzene |
| (1,1-Dimethylethyl)Benzene |
| 1-Methyl-2-n-propylbenzene |
| 1,4-Dimethyl-2-ethylbenzene |
| 1,3-Dimethyl-4-ethylbenzene |
| 1,2-Dimethyl-4-ethylbenzene |
| 1,3-Dimethyl-2-ethylbenzene |
| n-Undecane (hendecane) |
| 1,2-Dimethyl-3-ethylbenzene |
| 1,2,4,5-Tetramethylbenzene |
| 1,2,3,5-Tetramethylbenzene |
| C11 Aromatic |
| 2-Methylbutylbenzene |
| n-Pentylbenzene |
| 1-(1,1-Dimethylethyl)-3,5-(1,1-Dimethylethyl)Benzene |

VEHICLE EMISSIONS

| |
|-------------------------------------|
| Naphthalene |
| n-Dodecane |
| Alcohols (MLD Method #1001) |
| Methanol |
| Ethanol |
| Carbonyls (MLD Method #1004) |
| Formaldehyde |
| Acetaldehyde |
| Acrolein (Propenal) |
| Acetone (2-Propanone) |
| Propionaldehyde (Propanal) |
| Butyraldehyde (Butanal) |
| Methyl Ethyl Ketone |
| Methacrolein |
| Benzaldehyde |
| Crotonaldehyde |
| Valeraldehyde |
| m-Tolualdehyde |
| Hexanal |